

SOLUBILIZATION OF AN AUSTRALIAN BROWN COAL OXIDIZED WITH HYDROGEN PEROXIDE IN CONVENTIONALLY USED SOLVENTS AT ROOM TEMPERATURE

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INTRODUCTION

It is very important to develop effective methods for utilizing low rank coals such as brown coal and lignite, which are most abundant fossil resources. One of the inherent drawbacks for utilizing the coal lies in the difficulty of handling such as transportation and storage. To overcome the drawback, several methods for fluidifying the coal have been proposed. Preparation of coal-water mixture (CWM) is one of such methods, but low rank coals are not suitable for CWM preparation, because they have lots of hydrophilic functional groups such as -COOH and -OH. Liquefaction is another means to fluidify the low rank coals, but it is a technology of the next generation. Therefore, it would be very profitable if some practical methods which are suitable to fluidify low rank coals are developed. The authors have focused on the extraction of low rank coals in conventionally used solvents as one of such methods.

Extraction and swelling of coals by various solvents have been performed for decades as a means to examine the coal structure, but only the coals of a certain rank could be extracted by 70 wt% or so with a special solvent.¹ The extraction yield of low rank coals has been less than 10 wt% even in a highly polar solvents.¹⁻⁴ To increase the extraction yield of lower rank coals, several pretreatments of coals were performed.^{5,6} However, the treatments under severe conditions and/or in highly polar solvents are required to extract the low rank coal to a large extent. On the other hand, several researchers^{7,8} found that the coal was largely swollen with alcohol based binary solvents. We have recently found that an Australian brown coal oxidized by H_2O_2 for 2 h at 60°C was extracted at room temperature by 84 wt% in a mixed solvent of methanol and 1-methylnaphthalene.⁹

In this paper we performed the extraction of low rank coals modified by several oxidation methods in several combinations of low molecule alcohol and non-polar solvent systems to examine the validity of the proposed method. Then, the extraction mechanism of coal in the mixed solvents of methanol and non-polar solvents was discussed from the viewpoint of the change in coal structure and solvent properties.

EXPERIMENTAL

Oxidation of coal

Three kinds of coals, an Australian brown coal (Morwell, MW), a Canadian brown coal (Highvale, HV), and a Japanese sub-bituminous coal (Taiheiyō, TC) were used as raw coals. The coals were ground into fine particles of less than 74 μm , and dried in vacuo at 110°C for 24 h before use. The oxidation of the coals was performed as follows: 2 g of coal particles were mixed with 20 ml of 30% aqueous hydrogen peroxide (HPO) in a flask. After treating the mixture for 2 h in a water bath kept at a constant temperature of 25 °C or 60 °C, an excess of cold water was added to the flask to terminate the oxidation. The oxidized coals were filtrated and evacuated at 60 °C for 24 h. To examine the effect of the oxidation method, MW coal was also oxidized in an air stream at 250 °C (AO) using a thermogravimetric analyzer until no weight change was detected. The oxidized coals were abbreviated to (oxidation method)(treatment temperature).(treatment time(h)) such as HPO60.2 and AO250.2, etc.

Extraction of oxidized coals

The raw coals and the oxidized coals were extracted at 25°C by alcohol based binary solvents of m-xylene (m-X), 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), benzene (B), and tetralin (Tet), phenol (Ph) and tetrahydrofuran (THF). Methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH) and 2-methyl-1-propanol (2M1P) were used as the alcohols. The extraction was performed as follows: 200mg of the oxidized coal were mixed with 6 ml of solvent and were kept for 4h at 25 °C under the irradiation of an ultrasonic wave. After centrifuging the mixture and removing the extract, 6 ml of fresh solvent were added to the residue and the mixture was treated for 3 h at 25 °C under the irradiation of the ultrasonic wave. This centrifugation-extraction cycle was repeated three times. The residue was then washed with an excess of methanol and evacuated for 24 h at 60 °C. The extraction yield was calculated from the weight difference between the oxidized coal and the residue, and was represented on the basis of dry oxidized coal.

Characterization of the oxidized coal and their extracts

The change in coal properties through the oxidation was examined from the ultimate analysis, ^{13}C -n.m.r., TG-MS, and F.T.i.r. measurements. The extracts were dissolved by

DMF, then they were served to molecular weight distribution measurement using the GPC technique.

RESULTS AND DISCUSSION

Changes in coal properties through oxidation

The oxidation pretreatment was performed to change the coal into more extractable structure. However, the oxidation inevitably causes the loss of coal itself. Therefore, the degree of the oxidation must be optimized by taking into account both the extraction yield and the loss of coal. Then, the changes in the solid yield and the loss of coal through the oxidation were examined first. Table 1 lists the carbon conversions of the coals to solid, CO_2 , and water soluble organics through the oxidation. The ultimate analyses, and the atomic H/C and O/C values for the oxidized coals are also listed. When MW coal was oxidized by air for 4 h at 250°C (AO250.4), the carbon conversion to CO_2 was 0.20, indicating that 20% of carbon is lost through the oxidation. On the other hand, when MW coal was oxidized by H_2O_2 for 2 h at 60°C (HPO60.2), the carbon conversion to CO_2 was 0.04 and the carbon conversion to the water-soluble organics was 0.17. Since the water soluble organics can be recovered and utilized,¹⁰ the loss of coal was judged to be only 4% for HPO60.2 prepared from MW. This was also the case for HPO60.2 prepared from HV. These results indicate that the H_2O_2 pretreatment is superior to the air oxidation pretreatment from the viewpoint of minimizing the carbon loss through the pretreatment.

Then, the changes in coal properties through the H_2O_2 oxidation were examined in more detail from several analyses for MW coal. Both the H/C and O/C values of the solid increased through the oxidation for HPO25.4 and HPO60.2 as listed in Table 1. We have shown that both hydrogen and oxygen are introduced into the coal, mainly as the form of OH groups, through the H_2O_2 oxidation in a previous paper.¹⁰ This is peculiar to the H_2O_2 oxidation. Comparing the F.T.i.r. spectra between the oxidized coals and the raw coal, the amount of carboxyl groups was found to increase by the oxidation. Table 2 gives the carbon distributions estimated by the ^{13}C -n.m.r. for the raw coal and the HPO60.2. The amounts of COOH , O-aliphatic (including R-OH), and aliphatic carbon increased, on the contrary, the f_a value and the amounts of Ar-OH (including Ar-O-Ar), substituted and protonated carbons decreased through the H_2O_2 oxidation. From the above results, it was judged that the H_2O_2 oxidation decomposed a part of the covalent bondings such as Ar-OH, Ar-O-Ar, and substituted carbon, then produced -COOH , C-O-C and R-OH in the coal.

Extraction of oxidized coal by methanol and 1-methylnaphthalene mixtures

The solvent extraction of lower rank coals is believed to be affected by non-covalent interactions such as hydrogen bonding as well as the solubilization ability of the solvent.¹¹ The HPO60.2 prepared from MW coal was supposed to be enriched with the hydrogen bonding sites because of the increase in the oxygen functional groups. Therefore, the solvent suitable to extract the HPO60.2 must have the potential for breaking the hydrogen bonding in addition to the potential for dissolving the coal.

Methanol is known not to dissolve but swell coal to a large extent. On the other hand, two aromatic ring compounds such as naphthalene, naphthalene derivatives, etc., which are recovered from the coal conversion process, are judged to be solvents suitable to dissolve the coal, judging from the solubility parameter. This suggests that the extraction of the HPO60.2 is expected to be enhanced by using mixed solvents of methanol and aromatic compounds.

Figure 1 shows the extraction yields of the raw coal and the oxidized coals in a mixed solvent of methanol and 1-methylnaphthalene (1MN/MeOH). The abscissa in Fig.1 represents the volume fraction of methanol (f_v) in the mixed solvent. The extraction yield of the raw coal was 10 wt% at most at around $f_v=0.6$, and the extraction yield of HPO25.4 was slightly larger than that of the raw coal. The HPO60.2 was extracted little in pure methanol or pure 1MN, but was extracted to a large extent in the mixed solvent of $f_v=0.2$ to 0.9. At $f_v=0.56$ the extraction yield reached up to 84 wt% on the oxidized coal basis, which is comparable to the extraction yield in DMF. The value of 84 wt% on the oxidized coal basis corresponds to 66 wt% on the raw coal basis for HPO60.2. Even this value of the extraction yield is much larger than the values reported by now. If we add the water soluble organic acids recovered during the pretreatment to the extraction yield, the extraction yield reaches more than 80 wt% on the raw coal basis. The molecular weight distribution (number basis) of the 1MN/MeOH ($f_v=0.56$) extract of HPO60.2 ranged from 240 to 10000, and the average molecular weight was found to be 837.

Extraction of the oxidized coal by several mixtures of small molecule alcohols and solvents

Next, we examined the effect of the solvent type on the extraction of HPO60.2 prepared from MW. Figure 2 shows the extraction yields at 25°C in the mixed solvents of 1MN and several small molecule alcohols. The extraction yields in 1MN/EtOH, 1MN/PrOH were also as high as the extraction yields in 1MN/MeOH, but the maximum yield in 1MN/2M1P was

only 42 wt%. Since 2M1P has the largest molecule size of the alcohols tested, its penetration into the coal matrix would be retarded. Figure 3 shows the extraction yields of the HPO60.2 at 25 °C in the mixed solvents of MeOH and aromatic compounds. In 2MN/MeOH the HPO60.2 was also extracted to a large extent at $f_v=0.3$ to 0.9, and reached up to 80 wt% at $f_v=0.56$. However, in Xy/MeOH the HPO60.2 was extracted by only 33 wt% at maximum at $f_v=0.76$. This small extraction yield is probably due to less solubilization potential of m-xylene. On the other hand, the extraction yields of the HPO60.2 in the mixed solvents of methanol and THF or PhOH reached up to almost 80 wt% at $f_v=0.36$ in both binary solvents. The f_v value corresponding to the maximum extraction yield for these binary solvents was smaller than that in the mixed solvents of methanol and non-polar solvents.

Effect of coal type on the extractability of the oxidized coal

The H_2O_2 oxidation pretreatment was very effective to increase the solvent extraction yield for Morwell coal. To examine the effect of the H_2O_2 oxidation pretreatment for other coals, we extracted several coals oxidized by H_2O_2 for 2 h at 60 °C. Figure 4 compares the extraction yields of the oxidized coals in DMSO and 1MN/MeOH. The HPO60.2 prepared from MW coal was extracted more than 80 wt% in both DMSO and 1MN/MeOH as described above. For the HPO60.2 prepared from HV brown coal, the yield of DMSO-extract reached 82wt%, but the yield of 1MN/MeOH-extract was 48 wt%. For the HPO60.2 prepared from TC subbituminous coal, the extraction yields in 1MN/MeOH and DMSO were 30 wt% and 37wt%, respectively. The small extraction yield of TC coal was presumed to be due to a small extent of the oxidation. The solid yield through the H_2O_2 oxidation was 0.94 for TC as shown in Table 1. So, we oxidized the TC coal by H_2O_2 for 24h at 40 °C (HPO40.24) to increase the extent of oxidation. The solid yield through the oxidation was 80 wt%, whose value was almost same as that of HPO60.2 prepared from MW. The extraction yield of the HPO40.24 in DMSO increased up to 55 wt%, but not so large as that for the brown coals. These results suggest that the extraction yield of the coal oxidized by H_2O_2 in 1MN/MeOH is strongly dependent on coal type, and that the proposed method is more effective for lower rank coals.

Role of the binary solvent mixture on the extraction of the oxidized coal

The secondary interaction of brown coal is mainly due to hydrogen bonding and ionic force as reported by Nishioka.¹² Green et al.⁸ showed that the swelling ratio of coal increased in N-N-dimethylaniline and methanol mixture, and concluded that methanol could interact with the specific sites of the coal surface and break the hydrogen bonding. Lucht et al.¹³ and Suuberg et al.¹⁴ also claimed that methanol having a small molecule easily penetrated and swelled the coal to interact with the specific site of coal. Table 3 lists several properties of methanol, ethanol, DMF, DMSO, and pyridine. The values of relative dielectric constant for methanol and ethanol are as large as those for DMF and DMSO. The values of the hydrogen bond index summarized by van Krevelen¹⁵ and Guttman's ΔH for methanol and ethanol are larger than those for DMF, respectively. In addition methanol molecule is small and easy to penetrate into coal matrix as stated above. These discussion suggests that methanol well has a potential to break hydrogen bonding in coal.

Then the extraction mechanism of HPO60.2 prepared from MW in methanol based binary solvents was presumed as follows: Methanol disrupts the hydrogen bonding in the HPO60.2 and interacts with functional groups at first, then the penetration of aromatic compounds such as 1MN is enhanced. Since the aromatic compounds have the potential to solubilize the coal molecule interacting with methanol, the HPO60.2 could be extracted to a large extent. Then the solubilization of the methanol adducted coal may be regarded as the solubilization of the bituminous coal.

The regular solution theory may not be applied to the extraction of low rank coal,¹¹ but it seemed to be applicable to the extraction of the HPO60.2 in methanol based binary solvents, judging from the above discussion. Following the regular solution theory, the extraction yield is maximized when the solubility parameters of both coal and solvent are close together.¹⁵ Since the oxidized coal is adducted with methanol through its functional groups, the coal molecule would be enveloped by methanol molecules. Then, the solubility parameter of the HPO60.2 was calculated by taking into account the contribution of methanol adducted in terms of the following equation:¹⁶

$$\delta(\text{coal}) = \frac{7.0+63.5f_a+63.5(H/C)+106(O/C)+51.8(N+S/C)}{-10.9+12f_a+13.9(H/C)+5.5(O/C)-2.8((N+S)/C)} \quad (1)$$

Figure 5 shows the change in the solubility parameter of HPO60.2, $\delta(\text{HPO60.2})$, against the amount of methanol adducted. The $\delta(\text{HPO60.2})$ value decreased with the increase of the amount of methanol adducted. If it is assumed that methanol adducts with carboxyl groups first and then ArOH of HPO60.2, the $\delta(\text{HPO60.2})$ decreased from 13.1 to 11.5 first, and finally to 10.8 (cal/cm³)^{0.5} with the increase of the amount of methanol adducted.

The solubility parameter of the mixed solvent, δ , was calculated by ¹⁵

$$\delta^2 = \delta_d^2 + \delta_h^2 + \delta_p^2 \quad (2)$$

where δ_d , δ_h , and δ_p represent the solubility parameters deriving from dispersion forces, hydrogen bondings, and polar forces, respectively. The values of δ_d , δ_h , and δ_p are calculated from the values of pure solvents by

$$\delta_i^2 = x_1 \cdot \delta_{i1}^2 + (1 - x_1) \cdot \delta_{i2}^2 \quad (\delta_i: i = d, h, p) \quad (3)$$

where x_1 is the mole fraction of alcohol, and δ_{i1} and δ_{i2} are the solubility parameters of alcohol and nonpolar solvent, respectively.

Figure 6 shows the extraction yield of HPO60.2 at 25°C against the solubility parameter of the solvent calculated by eqs.(2) and (3). The δ (HPO60.2) value was assumed to change from 13.1 to 10.8 (cal/cm³)^{0.5} with the increase of the amount of methanol adducted as stated above. The extraction yield and the solubility parameter of the solvent correlated very well and the extraction yield reached a maximum at $\delta \approx 11.5$ (cal/cm³)^{0.5}. The value of 11.5 (cal/cm³)^{0.5} corresponded to the δ (HPO60.2) value calculated by assuming that methanol adducted with all carboxyl groups of HPO60.2. Thus the regular solution theory seemed to be applicable to the extraction of HPO60.2 with the alcohol based mixed solvent.

This supports the extraction mechanism mentioned above: Methanol and/or ethanol penetrate into the coal matrix easily, break the hydrogen bonding or ionic interaction in coal, and interact with the oxygen functional groups tightly. This facilitates the penetration of the binary solvent of non-polar solvent and alcohol. The macromolecules enveloped with alcohol will be easily extracted by the mixed solvent having strong solubilization potential. This may be speculative because the extraction behavior is also affected by the phase separation equilibrium among coal, binary solvent and extracts. We will examine the extraction behavior in more detail in future work. However, it is noteworthy that the regular solution theory hold unexpectedly for the extraction of the oxidized coal with alcohol based mixed solvents.

CONCLUSION

A new method was developed for extracting a great deal of brown coal at room temperature in conventionally used solvents. When an Australian brown coal, Morwell, was preoxidized with H₂O₂ for 2 h at 60 °C, the covalent bondings were partly decomposed and many carboxyl groups and C-O-C groups were formed. The oxidized coal was extracted in several alcohol based binary solvents. The maximum extraction yields of the oxidized coal surprisingly reached more than 80 wt% in the binary solvents of methanol/1-methylnaphthalene, ethanol/1-methylnaphthalene, methanol/2-methylnaphthalene, and methanol/phenol at an suitable alcohol fraction. The average molecular weight (number basis) of the extract was 837. The proposed extraction method will be useful to develop a new coal conversion method as well as to facilitate the transportation of coal.

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Table 1 Carbon conversions through the oxidation and ultimate analysis of oxidized coals.

Sample	Carbon conversion through oxidation			Ultimate analysis of the oxidized coal [wt%, daf]				mol ratio	
	acid	CO ₂	water soluble organics	C	H	N	O (diff)	O/C [-]	H/C [-]
MW Raw	1.00	-	-	64.0	4.7	0.7	30.6	0.359	0.881
HPO25.4	0.96	0.02	0.02	61.6	4.6	0.6	33.2	0.404	0.896
HPO60.2	0.79	0.04	0.17	60.1	4.9	0.7	34.3	0.428	0.978
A0250.4	0.80	0.20	0	68.4	3.8	1.0	26.8	0.294	0.666
HV Raw	1.00	-	-	67.0	4.3	1.0	27.7	0.310	0.770
HPO60.2	0.70	0.08	0.22	63.0	4.3	1.0	31.7	0.377	0.819
TC Raw	1.00	-	-	72.4	5.6	1.4	20.6	0.213	0.928
HPO60.2	0.94	0.02	0.04	71.3	5.9	1.5	21.3	0.224	0.993
HPO40.24	0.80	0.07	0.13	71.2	7.3	1.1	20.4	0.208	1.199

Table 2 Carbon distributions of Morwell coal and the H₂O₂ oxidized coal determined by ¹³C-n.m.r

sample	Raw	HPO60.2
Aromatic carbon		
H-C=O, =C=O	1.81	3.83
COOH	5.90	8.54
Ar-OH	9.01	6.93
Substitute	12.66	9.32
Protonated	34.09	24.55
Aliphatic carbon		
C-O-C	0.94	6.01
O-Methyl	1.63	3.69
Aliphatic	27.22	28.40
Methyl	6.73	8.73
total	36.53	46.83
Structural parameter		
f _h [-]	0.63	0.53
M ₀ [kg/kmol]	156.4	196.8

Table 3 Comparison of the solvent properties between alcohol and polar solvents

Solvent	Methanol	Ethanol	DMF	DMSO	Py	1MN	Xy
Relative dielectric constant	32.6	24.3	36.7	46.7	12.3	-	-
Guttman ΔH (=DN·AN/100)	7.8	7.4	5.7	5.8	4.5	-	-
Hydrogen bond index	8.9	8.9	6.4	-	8.7	-	-
Solubility Parameter							
δ (cal/cm ³) ^{0.5}	14.6	13.0	12.2	13.1	10.7	10.4	8.4
δ _D (cal/cm ³) ^{0.5}	7.6	7.7	8.5	9.2	9.3	10.4	8.3
δ _H (cal/cm ³) ^{0.5}	10.9	9.6	5.5	5.0	2.9	0.0	0.5
δ _P (cal/cm ³) ^{0.5}	6.1	4.3	6.7	8.0	4.3	0.2	0.5

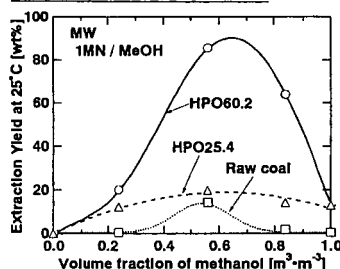


Figure 1 Extraction yield of the raw coal and H₂O₂ oxidized coal prepared from Morwell coal measured at 25°C in methanol and 1-methylnaphthalene mixture.

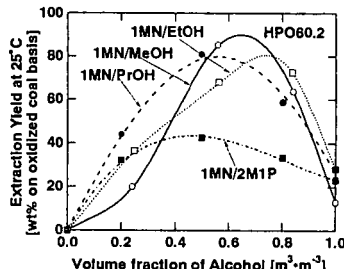


Figure 2 Extraction yield of the HPO60.2 prepared from Morwell coal measured at 25°C in the mixed solvents of several alcohols and 1-methylnaphthalene.

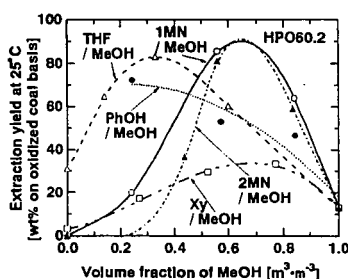


Figure 3 Extraction yield of the HPO60.2 prepared from Morwell coal measured at 25°C in various methanol based binary solvents.

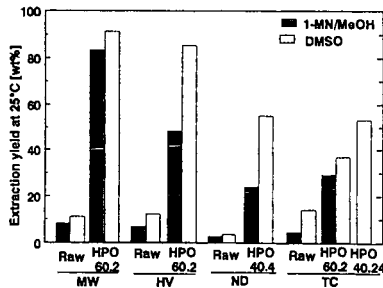


Figure 4 Effect of coal type on the extraction yield of the H₂O₂ oxidized coal.

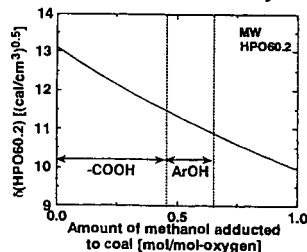


Figure 5 Change in the solubility parameter of HPO60.2 adducted with methanol.

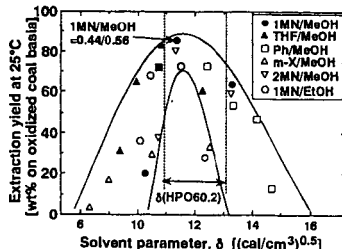


Figure 6 Relationship between the extraction yield of HPO60.2 prepared from Morwell coal and the solubility parameter of the solvent.